

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
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1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 25Nov02		3. REPORT TYPE AND DATES COVERED Final: 5/21/01 – 6/30/02
4. TITLE AND SUBTITLE AMBIENT REACTIVE SORPTION OF CW SIMULANTS ON CATION EXCHANGED ZEOLITES			5. FUNDING NUMBERS DAAD19-01-1-0620	
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9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSORING / MONITORING AGENCY REPORT NUMBER 41959.1-CH	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Zeolite sorbent/catalyst materials were prepared, characterized and then utilized to determine their surface interactions at ambient temperature with common CW simulants for VX and HD. From this research, new insights regarding reactive sorption pathways of simulants on exchanged zeolites at ambient temperature have been proposed which will aid in developing superior alternates for sorption and detoxification of CW agents in the field. Experiments utilized a Bomem FTIR spectrometer with Harrick cell for <i>in situ</i> measurements of interactions between zeolite and CW simulant. Zeolite Si/Al ratios were varied from 15 to 40. Three sorbent /catalyst media were evaluated (Chromium-ZSM-5, Silver-ZSM-5 and standard gamma alumina). Results showed maximum destruction of TCE and DEMP simulants by Chromium-ZSM-5, followed by Silver-ZSM-5. Gamma alumina was found to be the least destructive. Initial work with dichloropropene (DCP), which is a common pesticide and also a CW simulant showed ambient chemisorption and also chemical rearrangement on Chromium-ZSM-5.				
14. SUBJECT TERMS chemical warfare simulants, destruction, zeolites, ZSM-5, sorption, surface reaction, FTIR, filtration, decontamination			15. NUMBER OF PAGES 4	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED		20. LIMITATION OF ABSTRACT UL

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(Continuation Sheet)

1. **Publications:** No papers yet published, however an extensive presentation on interim results of this project was presented by the P.I. to scientific personnel at Edgewood Arsenal on January 24, 2002.

2. **Scientific Personnel supported by this project:**

Dr. Howard L. Greene, P.I., Principal Researcher, Ph.D., Cornell University, 1966

Dr. Philip W. Morrison, Co-P.I., Assoc. Prof., Ph.D., U. Calif.-Berkeley, 1987

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3. **Report of Inventions:** None

4. **Scientific Progress and Accomplishments:**

Scientific Procedures/Methodologies: Notice of award was received on June 12, 2001. As planned, a BS/MS student (M. Swanson) was recruited at that time to work on the project along with the two named investigators. Four different ZSM-5 zeolites were procured from UOP and Zeolyst with Si/Al ratios ranging from 15 (moderately hydrophilic) to 40 (moderately hydrophobic). Wet chemistry facilities for exchanging, filtering and calcining various cation-modified samples were set up in Rm. 4 and reagents for cation exchange, including chromium and silver salts were ordered and received. An order for the required Harrick *in situ* FTIR cell and temperature controller was placed, but was delayed by an 8-week delivery requirement. Review of pertinent FTIR literature and procedures commenced immediately so that preliminary ambient spectra could be obtained as soon as possible after arrival of the *in situ* cell. Simulants DEMP and CEPS and DCP were ordered and received from Aldrich; TCE was already on-hand.

The *in situ* FTIR cell and temperature controller were received at the end of August and were installed with the existing Bomem model MB151 FTIR. An existing HAL model 201 quadrupole mass spectrometer, capable of 10^{-7} Torr vacuum and 200 AMU analysis, was plumbed to the cell to supply vacuum and to aid in analysis of any simulant off-gas products. This system as originally plumbed was directly capable of vapor-dosing our prepared cation exchanged zeolite sorbents with TCE (trichloroethylene), the first low molecular weight volatile CW simulant studied. The FTIR *in situ* feature allowed analysis of the progress of surface reactions during ambient destruction of adsorbed simulant as a function of time. Cell temperature and pressure could also be varied during a run if desired. After initial experimentation, preparation of zeolite samples for exposure to CW simulants in the cell was improved by using a fine tungsten wire grid in which to embed the catalyst sample. When working with low volatility simulants, such as DEMP, the embedded catalyst sample was dosed (in the most recent runs) *in situ* using a very small simulant-wetted and tared sponge attached to a wire holder or by a microliter syringe. This method eliminated the need for aerosoling

any simulants and was found to deliver consistent doses of about 1 microliter to the embedded catalyst sample surface.

Zeolite samples for FTIR analysis were calcined in dry flowing air at 350°C for 3 hours and then outgassed at ambient temperature under vacuum ($\sim 10^{-7}$ Torr), also for 3 hours. For dosing with the TCE or DCP simulants, a dry nitrogen/TCE (or DCP) bubbler was employed to purge the cell. FTIR scans were initiated to document any evidence of catalyst surface sorption and surface reaction with the TCE or DCP. After a period of 30 minutes, the bubbler was disconnected and vacuum applied to the cell to remove any vapor phase TCE, DCP, or other non-adsorbed products, while FTIR scans continued to determine surface species and their changes with time. For FTIR runs using the low volatility simulants (DEMP, etc.) the dosing technique described in the previous paragraph was employed.

Research Accomplishments and Results: Ten zeolite samples have undergone cation exchange procedures (typically requiring about 4 days each) to give us an inventory of finished zeolites for the subsequent ambient FTIR - CW simulant study. The as-received and prepared samples were characterized to ensure that BET surface area (averaging about 360 m²/g) was not lost by dealumination during the exchange process. Cation levels for the chromium ZSM-5 (Cr-ZSM-5) and the silver ZSM-5 (Ag-ZSM-5) were determined using x-ray photoelectron spectroscopy (XPS). Chromium levels ranged from 0.36-0.79% as the Si/Al ratio went from 40 to 15, while silver levels went from 0.47 to 1.16% over the same Si/Al range. These acceptable values represent complete exchange of all Bronsted sites for the chromium samples, and about 60% of available sites for the silver samples. The lower exchange percent for silver samples may be due to its valence (+1) which requires a larger cation flux than chromium (valence +3).

To initially test the efficacy of the *in situ* experimental system, the FTIR cell was fitted with a Cr-ZSM-5 (Si/Al = 25) embedded tungsten grid as the sorbent/catalyst medium. Note that the Si/Al ratio is very important since it controls not only the number of exchangeable sites, but also the strength of those sites. Generally, as the Si/Al ratio increases, the number of active sites decreases, but the reactive strength of the remaining sites increases. So, more rapid and complete destruction of CW agents might be expected up to a point as Si/Al is increased, after which the potency of the overall catalyst diminishes because too few sites remain. Finding the optimum Si/Al ratio becomes an important experimental task that was not totally completed.

In the present study using the first simulant, the zeolite/grid sample was dosed *in situ* at ambient temperature with a chlorinated solvent, trichloroethylene (TCE) by means of a vapor generating bubbler. FTIR scans were immediately commenced on the closed cell and after about 30 minutes the cell was evacuated; FTIR scans were continued for a period of about 1 h. The scans showed rapid ambient sorption of the TCE followed by progressive ambient surface reactions as this relatively stable chlorinated solvent was significantly decomposed at ambient temperature in a matter of minutes. Products were aldehydes, carboxylates and a minor amount of CO₂ with corresponding reductions in heights of peaks denoting C=C, C-H, and C-Cl bonding. With Ag-ZSM-5, surface reaction was much less vigorous, with much lower amounts of oxygenated products. Application of vacuum caused substantial loss of most TCE peaks suggesting a lower affinity for the surface than with Cr-ZSM-5. The difference in activity with Cr versus Ag is probably due to the significant redox and oxygen-carrying abilities of Cr compared to Ag. Exposure of TCE to gamma alumina showed even less surface affinity for the TCE and even less reactivity on the surface than with the Ag-ZSM-5.

The second CW simulant to be investigated by FTIR techniques was diethylmethylphosphonate (DEMP). Again, the same three sorbent/catalyst media (Cr-ZSM-5, Ag-ZSM-5 and gamma alumina), all with Si/Al = 25, were utilized. Simulant dosing of the sample grid with this low volatility

compound was most recently accomplished by the second method described previously, using the tiny tared sponge (discussed above) to transfer known amounts of DEMP on to the grid-embedded catalyst surface. The FTIR spectrum for DEMP has major characteristic spectral features at wavenumbers of 1269 (P=O), 1045 and 961 (P-O) and 1384, 1316, and 900 (P-CH₃). With DEMP applied to Cr-ZSM-5, the P=O peak at 1269 immediately began to diminish and after about 3.6 minutes was lost. The P-O peaks at 1045 and 961 were also reduced substantially, but even after about 30 minutes exposure, small remnants of these peaks remained. Conversely, the P-CH₃ peaks at 1384, 1316 and 900 appeared to remain substantially intact throughout the exposure indicating little bond breakage here. Evacuating the cell made no visual difference in the spectrum since DEMP's low volatility keeps it in the liquid phase throughout the experiment. With DEMP on Ag-ZSM-5, attack of the P=O bond was much slower, requiring about 20 minutes before it was finally lost. Attack of the P-O bonds by Ag-ZSM-5 proceeded almost as rapidly as with Cr-ZSM-5, but again with remnant peaks remaining after 20 minutes exposure. DEMP applied to the gamma alumina sample showed by far the least chemical rearrangement over time. Here, we observed a shift in the P=O bond, but no diminishment in amount, and only minor changes in the P-O spectral features, suggesting very little reactivity. In addition, there was no measurable reduction in the peaks representing the P-CH₃ bonds.

Several preliminary runs using a Cr-ZSM-5 zeolite with higher Si/Al ratio (40 versus 25), along with earlier data at Si/Al of 15, have shown a consistent increase in the rate and severity of chemical rearrangement for DEMP with increasing Si/Al ratio. This suggests that stronger sites, even though less numerous, will improve simulant destruction results.

Also, because of the potential health hazard of using chromium as the exchanged cation, several preliminary scoping runs with both the H⁺ and the Fe⁺⁺ forms of exchanged ZSM-5 (more environmentally friendly) were carried out. Because no XPS data are available on these sorbent/catalysts, and surface reaction results have not been quantified by repetition, results must be considered tentative. However, with both of these forms, significant surface rearrangement of DEMP was noted which is very encouraging.

Efforts were made to develop an improved sample preparation method for low volatility simulants that involved a KBr pellet with dispersed zeolite contacting a second pellet coated with the simulant. This method eventually proved unreliable because of sample non-uniformity and was discontinued.

The most recent work involved ambient reaction of the vapor phase pesticide DCP on a KBr pellet coated with dispersed zeolite. By careful adjustment of zeolite amount and DCP concentration, spectra with time have been obtained which appear to show abstraction of hydrogen and chlorine with simultaneous formation of new peaks, some likely containing oxygen in the form of aldehydes. More analysis of these data still needs to be done.